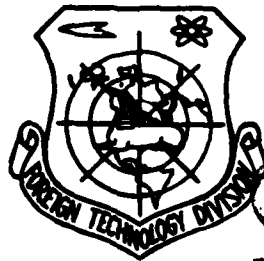# FOREIGN TECHNOLOGY DIVISION

CALCULATION OF THE ENERGETIC CHARACTERISTICS OF TN IN COMPOSITE
SOLID PROPELLANTS

by

Zhang Wei and Tian Deyu

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Calculation of the Energetic Characteristics of TN in Composite Solid Propellants

Zhang Wei and Tian Deyu

Abstract

This paper introduces the physiochemical properties of a new organic oxidizer - 2, 3, 5, 6 - tetranitrato - 1,4 - Dinitropiperazine (TN). Based on White's minimization of Gibbs free energy principle, its energetic characteristics in solid propellants are investigated with the aid of a computer. The results indicate that the theoretical specific thrust of a composite solid propellant consisting of TN, aluminum powder (Al) and HTPB can reach 276 sec, approximately 10 sec. higher than the Ap,Al and HTPB series of propellants. This demonstrates that TN is indeed a high energy oxidizer. In addition, characteristics of smokeless propellants consisting of TN and HTPB are being studied preliminarily in this paper.

Introduction

Propellant is an energy source for a space craft. According to the rocket range equation and the final velocity formula for the active section

$$v_k = I_s \cdot g \cdot \ln(1 + W_o/W_k)$$
$$X_a = 2S_i + K \cdot v_k^2 \tag{1}$$

where v_k is the maximum final velocity of the active segment of the rocket;

1

I_s is the specific thrust of the propellant;

W_p and W_k are the weight of the propellant and the structural weight of the engine, respectively;

S_0 is the range of the active section;

g is the gravitational acceleration; and

K is a constant

One can see that the range of the rocket is proportional to the specific thrust. On the other hand, when the range and other parameters are fixed, the amount of propellant can be reduced with increasing specific thrust, resulting in the reduction of the weight of the engine. Therefore, to investigate ways and methods to improve the energy of the propellant has a very important significance in the development of the aerospace industry. One of the primary methods to raise the energy of the propellant is to include highly energetic materials in the propellant to the extent possible, such as energetic oxidizers and binders. This paper discusses a theoretical study of the energetic characteristics of a new energetic oxidizer TN in solid propellants.

In the seventies, Wang Zenghui and Tien Deyu designed and successfully synthesized 2,3,5,6 - tetranitrato - 1,4 dinitropiperazine (TN) in China. As compared to the commonly used oxidizer ammonium perchlorate (Ap), it has advantages such as absence of chloride and high energy. To date, it has not been reported in the literature. The physicochemical properties of TN are briefly introduced in this paper. Based on the minimization of Gibbs free energy principle by White, a computer program is compiled in FORTRAN and run on a DPS-6 computer to calculate the
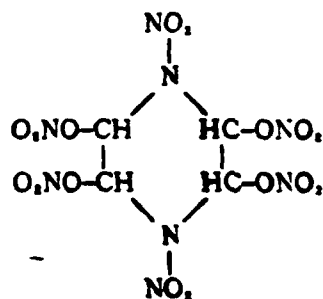
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energetic

characteristics of composite solid propellants consisting of HTPB[/85]
(Hydroxytetrapolybutadiene)-TN, HTPB-Al-TN and HTPB-Al-Ap-TN.
Parameters such as the theoretical specific thrust (I_{sp}),
characteristic velocity (c*), combustion chamber temperature (T_c)
and combustion products are obtained. In addition, some patterns
are found. Among the HTPB-TN propellants, when the weight ratio
of TN to HTPB is 9:1, the theoretical specific thrust reaches its
maximum of 269.33 sec. In the HTPB-TN-Ap-Al series, the energy
indicator increases with increasing TN content. If TN is used to
totally replace Ap, I_{sp} can be increased by 10 sec. Based on
this TN is indeed a high energy organic oxidizer which is
worthwhile to be further investigated.

II. Brief Introduction to the Physicochemical Properties of

2, 3, 5, 6-Tetranitrato - 1,4 Dinitropiperazine

TN is a new high energy organic oxidizer. The synthesized
TN appears to be white short cylindrical crystals. Its melting
point is 138 ~ 140°C. Through elemental analysis, infrared
spectroscopy and nuclear magnetic resonance, its chemical formula
is proven to be $C_4H_4N_8O_{16}$. Its structure is

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$$
\begin{array}{c}
\text{NO}_2 \\
| \\
\text{N} \\
\diagup \quad \diagdown \\
\text{O}_2\text{NO--CH} \qquad \text{HC--ONO}_2 \\
| \qquad\qquad | \\
\text{O}_2\text{NO--CH} \qquad \text{HC--ONO}_2 \\
\diagdown \quad \diagup \\
\text{N} \\
| \\
\text{NO}_2
\end{array}
$$

The heat of combustion is -4647.17 kJ/kg and its heat of
formation is -220.62 kJ/mole (-525.26 kJ/kg). Its specific
gravity d_{20}^{20} is 1.812. The theoretical oxygen content is 60.95%.
The oxygen content per unit volume is 1.105 g/cm^3, which is close
to that of liquid oxygen (the oxygen content per unit volume is
1.14g/cm^3 for liquid oxygen).

III. Energetic Characteristics of TN in Solid Propellants

A computer program is compiled in FORTRAN based on
White's principle of minimization of Gibbs free energy to
calculate energetic parameters such as the theoretical specific
thrust I_{sp}, combustion chamber temperature T_c, and the average
molecular weight $\bar{M}_{gc}$ of the gaseous product. The calculated
results were found to be very close to the values reported in the
literature[2]. The theoretical specific thrust only fluctuates
within the range of 1 sec, as shown in Table 1. Thus, we proved
that the algorithm and the program are accurate and reliable.

The scope of this discussion is limited to simple propellant
systems consisting of oxidizers, binders and metallic additives,

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assuming that the minor constituents would not significantly affect the energetic characteristics. The properties of the compounds used are briefly listed in Table 2.

We chose HTPB as the binder and calculated the energetic parameters of three systems:

1. Effect of TN and Al Contents in the TN-HTPB-Al Series on Its Energetic Characteristics

When the HTPB content is fixed (11%), the energy of the propellant increases with increasing aluminum content (the content of TN also decreases correspondingly). As the aluminum content increases by 20%, the theoretical specific thrust increases by 7 sec, the combustion chamber temperature goes up by 680K, and the characteristic velocity increases by 48 in/sec, as shown in Table 3 and Figure 1. The calculated results show that with increasing combustion chamber temperature T_c, the theoretical specific thrust I_{sp} and characteristics velocity C* rise. As the mean molecular weight of the combustion product /86 increases, the theoretical specific thrust and characteristic velocity decrease. The effect of the adiabetic index is not significant, which is consistent with the following equation.

$$I_s \propto \sqrt{T_c / \overline{M}_{gc}}$$

where $\overline{M}_g$ is the mean molecular weight of the gaseous product.

Table 1. Comparison of Energetic Parameters Calculated Using
the Computer Program and Values Reported in the
Literature[L]

1. 序号	2. 配 方 (%)			3. 计算方法	4. 能 量 示 性 数		
	Ap	PV	Al		$I_{sp}(S)$	$T_c(K)$	n
1	95	5	—	本 法 5	219.58	2541.51	27.45
				文献法 6	219	2529	27.47
2	90	10	—	本 法 7	252.16	3014.8	28.10
				文献法 8	252	3013	28.13
3	80	20	—	本 法 9	221.06	2054.98	29.43
				文献法 10	221	2036	29.43
4	81	9	10	本 法 11	280.99	3432.9	28.52
				文献法 12	281	3433	28.54
5	76.5	8.5	15	本 法 13	283.82	3826.8	29.81
				文献法 14	284	3821	29.83

15. 注: PV为聚乙烯

1.   number
2.   formulation (%)
3.   method of calculation
4.   energetic parameters
5.   this method
6.   method in the literature
7.   this method
8.   method in the literature
9.   this method
10. method in the literature
11. this method
12. method in the literature
13. this method
14. method in the literature
15. Note: PV is polyvinyl

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Table 2.   Brief Properties of Compounds Used

1. 化 合 物 名 称	2. 代 号	3. 化 学 式	4. 密 度 (g/cm³)	5. 生 成 热	
				kJ/kg	kcal/kg
6. 2,3,5,6-四硝胺脂-1,4-二硝基哌柔	TN	$C_4H_4N_8O_{16}$	1.812	−525.26	−125.54
7. 过 氯 酸 铵	Ap	NH_4ClO_4	1.95	−2471.95	−590.81
8. 铝 粉	Al	Al	2.7	0	0
9. 端羟基聚丁二烯	HTPB (R-45M)	$C_6H_{9.695}O_{0.095}$	0.93	−19.04	−4.55
10. 聚 乙 烯	PV	$(CH_2)_n$	0.92	−1917.95	−458.4

1. compound
2. symbol
3. chemical formula
4. density (g/cm³)
5. heat of formation
6. 2, 3, 5, 6 - tetranitrato - 1,4 - dinitropiperazine
7. ammonium perchlorate
8. aluminum powder
9. HTPB
10. polyvinyl

Table 3. Effect of Various TN and Al Contents on the Energetic Parameters of Propellants

1.	2. 方 (%)			3. 能量示 数				
号	TN	Al	HTPB	I_{sp}(S)	T_c(K)	$\bar{M}_{gc}$	C^*(m/s)	k
1	8·	0	11	269.04	3475.4	26.96	1614.2	1.1579
2	8·	5	11	271.34	3646.1	25.20	1629.7	1.1557
3	79	10	11	273.42	3821.6	23.30	1644.2	1.1539
4	74	15	11	275.22	3999.6	21.30	1657.5	1.1526
5	72	17	11	275.83	4066.2	20.49	1661.8	1.1511
6	69	20	11	276.01	4155.6	19.55	1661.9	1.1450

4. 注: $\bar{M}_{gc}$为产物中气体的平均分子量

1. number
2. formulation (%)
3. energetic parameters
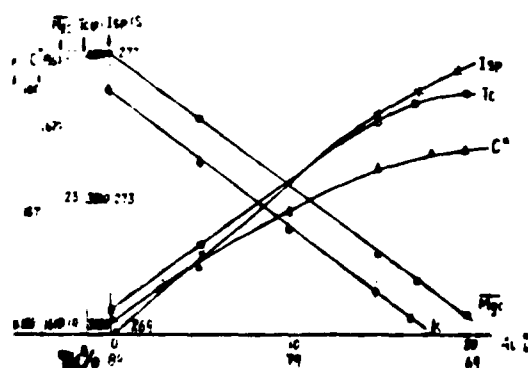4. Note: $\bar{M}_{gc}$ is the average molecular weight of the gaseous product.

Figure 1. Effect of Varying TN and Al Contents on the Energetic Characteristics

2. Effect of Varying TN and Ap Contents on the Energetic
Characteristics of the TN-Ap-Al-HTPB System

When the HTPB and Al contents are fixed (11% for HTPB and
16% for Al), the energy of the propellant increases with
increasing TN content (the content of Ap decreases
correspondingly). When the content of TN increases by 1%, on the
average, the specific thrust increases by 0.15 sec, the
combustion chamber temperature goes up by 5.6K and the
characteristic velocity increases by 0.93 m/sec. If Ap is
completely replaced by TN in the formulation, I_{sp} will increase
by approximately 10 sec. as compared to that of a propellant
without any TN. The calculated results are shown in Table 4 and
Figure 2.

Table 4. Effect of Varying TN and Ap Contents on the Energetic
Parameters of the Propellant

1. 宋	2. 三 方 (%)				3 能 量 示 性 数			
号	TN	Ap	Al	HTPB	I_{sp}(S)	T_c(K)	O.B(%)	C^*(m/s)
1	70	3	16	11	275.05	4012.3	−32.34	1656.6
2	65	8	16	11	274.25	3978.1	−31.79	1651.4
3	60	13	16	11	273.47	3945.6	−31.23	1646.3
4	50	23	16	11	271.95	3884.5	−30.11	1636.6
5	40	33	16	11	270.50	3827.2	−28.99	1627.8
6	30	43	16	11	269.04	3773.4	−27.87	1617.8
7	20	53	16	11	267.58	3722.1	−26.75	1608.8
8	10	63	16	11	266.12	3672.6	−25.63	1600.0
9	5	68	16	11	265.38	3648.5	−25.07	1595.6
10	0	73	16	11	264.60	3634.6	−24.51	1591.3

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1. number
2. formulation (%)
3. energetic parameters

As we all know the higher the sum of the heat of formation   /88
of each constituent of the propellant is, the higher the energy
is.

$$\Delta H_{combustion} = \Delta H_{product} - \Delta H_{propellant}$$

where $\Delta H_{combustion}$, $\Delta H_{product}$ and $\Delta H_{propellant}$ are the exotherm
of propellant combustion, the formation heat of the product and
the heat of formation of the constituents of the propellant,
respectively. The heat of formation of TN is larger than that of
Ap. Therefore, increasing TN content will improve the energy
content. From the structure of the compound, TN contains more
highly energetic functional groups, such as $-NNO_2$ and $-ONO_2$, and does
not contain Cl. Hence, the energy of TN is higher than that of
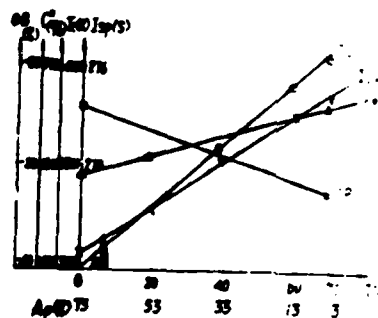Ap. The calculated results also verified this point.

Figure 2. Effect of Varying TN and Ap Contents on the Energetic
           Characteristics

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3. Effect of Varying Contents of TN and HTPB on the Energetic Characteristics of the TN-HTPB Smokeless Propellant System

With increasing TN (and correspondingly decreasing HTPB), the theoretical specific thrust (I_{sp}) and characteristic velocity (C*) will rapidly increase. As TN is increased from 80% to 90%, I_{sp} is increased from 247.96 sec to 269.33 sec. I_{sp} is increased by 21.4 sec. When TN content continues to increase, energetic parameters such as I_{sp} begin to decrease gradually. When the TN content is 90%, the theoretical specific thrust I_{sp} has its maximum, as shown in Table 5 and Figure 3. The oxygen balance of the propellant at the maximum is -11.4%.

Table 5. Energetic Parameters of the TN-HTPB Series of Smokeless Propellants

1. 序号	2. 配 方 (%)		3. 能 量 示 性 数			
	TN	HTPB	I_{sp}(s)	T_c(K)	C*(m/s)	O.B(%)
1	100	0	233.21	3086.3	1405.0	22.9
2	95	5	258.74	3401.5	1543.5	5.7
3	92	8	267.30	3477.1	1595.2	−4.5
4	91	9	268.79	3486.0	1604.8	−7.9
5	90	10	269.33	3485.9	1610.5	−11.4
6	89	11	269.04	3475.4	1614.2	−14.8
7	88	12	268.10	3453.0	1616.1	−18.2
8	86	14	264.75	3356.5	1613.5	−25.1
9	84	16	260.05	3217.8	1600.9	−31.9
10	82	18	254.39	3024.6	1578.6	−38.8
11	80	20	247.96	2805.9	1548.1	−45.6

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1. number
2. formulation (%)
3. energetic parameters

Based on the calculated results, the CO_2 content in the product increases rapidly with increasing TN content. The contents of H_2O and CO will decrease and the heat released in the combustion will increase. The temperature of combustion will increase, leading to an increasing specific thrust. When the content of TN is excessively high, the degree of oxidation of the product increases, i.e., the content of CO_2 and O_z increases; once the TN content exceeds 90% the content of O_2, in particular, increases significantly. The combustion temperature will drop. In addition, due to an increase of complex molecules such as CO_2 and O_2 in the product, the mean molecular weight of the product increases, causing the specific thrust to drop rapidly as shown in Table 6 and Figure 4.

Table 6. Specific Thrust and Combustion Product of the TN-HTPB /89
Series of Smokeless Propellants

1.	2.		3.	4.			(mole/kg)	
	TN	HTPB	I_{sp}(s)	CO	CO_2	H_2O	O_2	N_2
1	...	0	233.21	1.0001	8.5198	4.2584	6.8104	8.9924
2	95	5	258.74	4.1382	8.5448	6.0690	3.0199	8.5707
3	92	8	267.30	6.7658	7.8144	7.0856	1.4945	8.4056
4	91	9	268.79	7.7470	7.4646	7.3990	1.1078	8.3580
5	90	10	269.33	8.7820	7.0630	7.6990	0.7837	8.3122
6	89	11	269.06	9.8663	6.6110	7.9485	0.5228	8.2666
7	88	12	268.10	10.9972	6.1125	8.1601	0.3241	8.2191
8	86	14	264.75	13.3606	5.0136	8.3628	0.0939	8.1095

1. number
2. formulation (%)
3. specific thrust
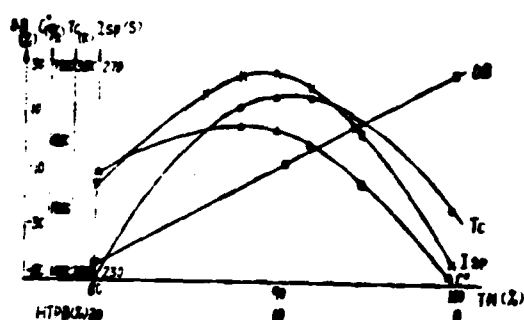4. combustion products (mole/kg)

Figure 3. Effect of Varying HTPB and TN Contents on the
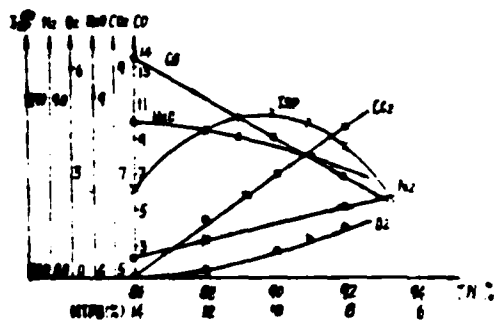Energetic Characteristics

Figure 4.   Effect of Varying HTPB and TN Contents on the Specific
Thrust and Combustion Products

The composite smokeless propellant consisting of HTPB and TN
does not contain elements such as Al and Cl. Thus, the smoke is
drastically reduced during combustion, which satisfies the
practical requirements of engines for satellites, spacecraft and
tactical rockets. As compared to propellants containing Al and
Cl, it has the advantages of low combustion temperature, less
engine nozzle erosion, lower mean combustion gas molecular
weight, absence of two phase loss and high energy efficiency.

Because the effective oxygen content of TN is high and its
own energy content is also high, therefore, we used TN to replace
the oxidizer ammonium chloride in the smokeless propellant. In
addition, we performed a calculation for this system. The
results showed that the addition of TN can greatly improve the
specific thrust of the propellant. The maximum specific thrust

is close to that of the propellant containing aluminum and Ap. Based on the above calculation and discussion, theoretically speaking, TN is an energetic organic oxidizer.

IV. Conclusions

The nitrogen content of 2, 3, 5, 6 - tetranitrato - 1,4 dinitropiperazine is 26.67 % and its oxygen content (61%) is high. Its specific gravity is relatively large. The volumetric oxygen content (1.105 g/cm^3) is close to that of liquid oxygen. The theoretical specific thrust of this single component propellant is 233.21 sec. The specific thrust of a smokeless /90 propellant containing TN and HTPB increases with increasing TN content. When the TN content is 90%, the maximum theoretical specific thrust can reach 269.33 sec and the characteristic velocity C* can be as high as 1610.5 m/sec. The theoretical specific thrust of a composite solid propellant consisting of TN, HTPB and Al could reach 276 sec and the characteristic velocity could reach 1662 m/sec.

Among propellants consisting of HTPB-Al-TN-Ap, when the contents of HTPB and Al are fixed, the specific thrust increases with increasing TN (and decreasing Ap). Its values vary between 265 ~ 275 sec.

We can conclude from the above discussion that energetic oxidizers and other energetic components of the propellant can improve its energy content.

From the energy angle, the contribution of TN as an oxidizer to the energy of the propellant is discussed theoretically in

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this paper. The calculated results indicate that, because the oxygen content of TN itself is higher than that of Ap and it is an energetic oxidizer, therefore, the use of TN to replace Ap as the oxidizer can increase the energy of the propellant. In addition, because TN does not contain Cl, it can also be used in smokeless propellants.

The authors wish to express their gratitude to Associate Professor Jiang Yu for his assistance during the writing of this paper.

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[2] Barrel Siegeland and Leory Schleler, Energetic of Propellant Chemistry, 1964.

CALCULATED RESEARCH ON THE ENERGETIC CHARACTERISTIC OF TN IN COMPOSITE SOLID PROPELLANT

Zhang Wei   Tian Deyu

Abstract

This paper discussed briefly the properties of a new organic oxidizer—2,3,5,6–Tetranitrato–1,4–Dinitropiperazine (TN). on the basis of the method of White's Minimization of Gibbs Free Energy, we also studied the energetic characteristics of TN in Composite Solid Propellant by means of electronic computer. The calculated results show thatthe theoretic specific impulse of the system of TN, Al and HTPB reaches 276 seconds, about ten seconds higher than the system of AP, Al and HTPB. This shows that TN does act as a high energetic oxidizer. The paper also did an initial research on the energetic characteristics of composite solid smokeless propellant consisted of TN and HTPB.